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Structural organization of catalytic functions in Mo-based oxides for propane selective oxidation

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Abstract

Several single phasic Mo–V–O-based mixed oxides, all of which have a layer structure in the direction of *c*-axis and a high dimensional arrangement of metal octahedra in *a–b* plane, were synthesized by hydrothermal method and their catalytic performance in the selective oxidation of propane to acrylic acid were compared in order to elucidate structure effects on catalytic property and roles of constituent elements. It was clearly demonstrated that the catalyst with the particular arrangement of MO_6 (M = Mo, V) octahedra forming slabs with pentagonal, hexagonal and heptagonal rings in (0 0 1) plane of orthorhombic structure was exclusively superior both in the propane oxidation activity and in the selectivity to acrylic acid to the other related Mo- and V-based layer oxide catalysts consisting of either pentagonal or hexagonal ring unit. The role of constituent elements was clarified by the comparison of catalytic performance of MoVO, MoVTeO and MoVTeNbO, all of which have the same orthorhombic structure. Mo and V, which were indispensable elements for the structure formation, were found to be responsible for the catalytic activity for propane oxidation. Te located in the central position of the hexagonal ring promoted the conversion of intermediate propene effectively, resulting in a high selectivity to acrylic acid. The introduced Nb occupied the same structural position of V and the resulting catalyst clearly showed the improved selectively to acrylic acid particularly at high conversion region, because the further oxidation of acrylic acid to CO_x was suppressed.

Keywords: Mo–V–O-based complex oxide catalysts; Selective oxidation of propane to acrylic acid; Hydrothermal synthesis; Structural effects on catalytic performance; Role of constituent elements

1. Introduction

The selective oxidation of light alkanes into oxygenated products is a very attractive way for the chemical utilization of natural gas resources. Propane selective oxidation is one of the recent challenges in selective oxidation field [1]. The one-step direct conversion to acrylic acid has especially attracted many research interests with a view to replace the current two-steps propene-to-acrolein and acrolein-to-acrylic acid process. The most promising catalyst up-to-date is a MoVTeNbO mixed oxide developed by Mitsubishi Chemicals and is reported to be able to achieve more than 40% of acrylic acid yield [2]. However, due to the difficulty in the preparation of this catalyst, a little information was reported about how this multicomponent catalyst works [3–7].

After the development of the MoVTeNbO catalysts which have been prepared by conventional dry-up method, we have succeeded in preparing the Mo–V–O-based catalysts by hydrothermal method [4]. And recently we found that this method was applicable for the syntheses of single phasic binary MoVO, ternary MoVTeO and quaternary MoVTeNbO complex metal oxides. Particularly, the synthesis of binary MoVO having the same crystal structure of the orthorhombic MoVTeO and MoVTeNbO was done for the first time [8].

Here in this work we conducted hydrothermal preparations of various Mo-based complex metal oxides having different crystal structures and different elemental compositions, all of which were tested as catalysts for the selective oxidation of propane to acrylic acid and compared in their catalytic performance. Based on the data we deduce structure–activity relationship and the role of each element of the MoVTeNbO catalyst in the propane oxidation.

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2. Experimental

Hydrothermal conditions used for synthesizing the orthorhombic MoV(Te)(Nb)O mixed oxides are following. Using ammonium heptamolybate, vanadyl sulfate, tellurium oxide (or telluric acid for MoVTeNbO) and niobium oxalate as starting materials, a slurry was prepared by mixing the desired chemicals in an appropriate ratio and was then introduced into a stainless steel autoclave equipped with a Teflon inner tube. The hydrothermal reaction was carried out at 175 °C for 20, 48 and 72 h for MoVO, MoVTeNbO and MoVTeO, respectively. The produced black solids were separated by filtration, washed with distilled water, dried in air at 80 °C overnight and finally calcined under N_2 stream (50 ml/min) for 2 h at 600 °C (500 °C for binary MoVO) as we have already reported previously [8,9]. MoVTeO was precalcined in air at 280 °C for 2 h in a muffled furnace before the calcination in N_2. The Mo-based mixed oxides having related crystal structure (Table 1) were prepared by usual dry-up or solid state reaction methods described in the literature [10–12]. The structure of the catalysts was characterized by XRD (Cu Kα) analysis. The compositions in each element in the bulk and on the surface were determined by ICP and XPS, respectively. Specific surface area was measured by N_2 adsorption at 77 K using BET method.

Propane and propene oxidations in gas phase were carried out at an atmospheric pressure in a conventional flow system with a fixed bed tubular reactor (Pyrex) in the temperature range of 280–420 °C at a space velocity of 2400 and 9600 ml/min/g cat. for propane and propene, respectively. The feed composition was: $C_3H_8(C_3H_6)/O_2/N_2/H_2O = 8(3)/10/37(42)/45$ (%). Both reactants and products were analyzed by online GC system.

3. Results and discussion

3.1. Structure dependency of the catalytic activity

Fig. 1 illustrates the model crystal structures of four distinct types of Mo-based oxides. All of them assume basically the same layered structure, in which networks of corner-shared MO_6 (M = Mo, V) octahedra form slabs and the octahedra between the slabs also share the corner oxygen forming linear infinite chains of octahedra along c-direction. The unit cell parameters of c-axis are always 4 Å for every case in this layer-type structure. The difference in each structure is the octahedra arrangement in the slabs as can be seen in Fig. 1. In the orthorhombic structure as described in Fig. 1(1), the MO_6 (M = Mo, V) octahedron network in the slab is constructed with pentagonal and hexagonal rings of the octahedra. In this case the heptagonal rings are generated during the linking of these pentagonal and hexagonal rings [13]. The pentagonal bipyramidal sites may be occupied by Mo and V. Te as the third constituent element is located in hexagonal channels exclusively [6], whereas the heptagonal channels remain empty. It has been revealed that Te in the hexagonal channel was linked together with oxygen along c-axis [6].

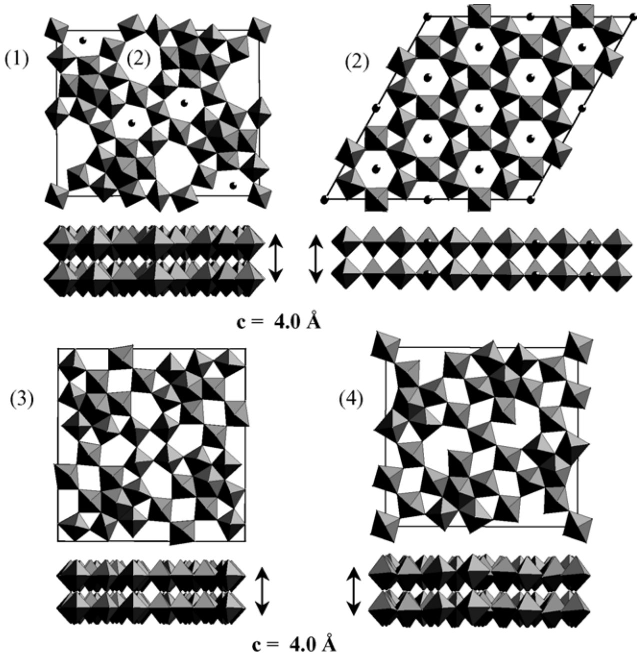

Fig. 1. Structural models of layered Mo-based complex metal oxide catalysts along [0 0 1] and [1 0 0] directions, (1) orthorhombic MoV(Te)(Nb)O, (2) hexagonal MoV(Te)(Nb)O, (3) tetragonal $(Mo, V)_5O_{14}$ and (4) orthorhombic $Mo_{17}O_{47}$. (●), Te sitting in hexagonal channel.

The other structures are rather simple and not possessing the heptagonal rings; the hexagonal phase contains only hexagonal ring channels (Fig. 1(2)) [10], whereas Mo_5O_{14} in the tetragonal phase (Fig. 1(3)) contains the pentagonal ring channels mainly [11]. The $Mo_{17}O_{47}$ material, which is a kind of analogue of Mo_5O_{14}, also contains the pentagonal ring channels mainly as shown in Fig. 1(4)) [12].

Table 1 summarizes the activity of these catalysts except $Mo_{17}O_{47}$ in the propane and propene oxidations. The superior catalytic activity of the orthorhombic material in both propane and propene selective oxidations was clear, compared to the other Mo-based layer oxide catalysts. As mentioned above, all these catalysts present the same arrangement of the octahedra along c-axis with common c-parameter of 4.0 Å (Fig. 1). However, their catalytic behaviour was completely different. In addition, the

Table 1
Catalytic activity of Mo–V–O-based oxides for C_3 oxidations

Catalysts[a]	Structure	Conversion[b] (%)	
		C_3H_8	C_3H_6
MoVTeO	Othorhombic	33	68
MoVTeO(h)	Hexagonal	1	9
MoVO(t)	Tetragonal(Mo_5O_{14})	0	6

[a] Catalyst bulk compositions: MoVTeO, $Mo_{1.0}V_{0.44}Te_{0.1}O$; MoVTeO(h), $Mo_{1.0}V_{0.81}Te_{0.64}O_x$; MoVO(t), $Mo_{1.0}V_{0.25}O_x$.

[b] Reaction temperature: 380 °C.

catalysts always needed grinding before catalytic use to be active and selective for the reactions, because the catalyst particles were rod-shaped crystalline which was long in the *c*-direction, as ascertained by SAED analysis. It can be simply considered that the grinding increased the exposed surface of *a–b* plane. All these results, therefore, clearly emphasize that the slab plane with the particular arrangement of the octahedra only possesses the high catalytic activity and selectivity for the propane oxidation.

As described above, the orthorhombic Mo–V–O-based catalyst is not a simple structural mixture of the phase constructed with the pentagonal ring unit and the phase with the hexagonal ring unit but is a new structural material with the additional heptagonal ring. It might be, therefore, natural to assume that the heptagonal ring unit creates active sites for propane oxidation. Although it is reported that the heptagonal ring is empty, we speculate that there may exist protons in the ring, because ammonium cation has always observed by IR in the fresh MoVTeO(ortho) sample and disappeared after the heat-treatments [14]. We believe that this additional acidic function would play a role in the course of the propane oxidative activation.

The other point that may affect the catalytic activity is concerned about the situation of octahedral coordination. To form the orthorhombic phase with the complicated arrangement of the pentagonal and hexagonal rings in the slab, the octahedra in the structure must be distorted or puckered, compared to the other structural phases which are rather symmetric. In fact, a recent reported on the structure revealed the distortion of the octahedra in the same catalysts [4]. The distorted state may give rise to active lattice oxygens and also may facilitate the migration of lattice oxygen in the lattice, which is obviously suitable for achieving high and stable oxidation activity.

No matter which functions involve, it is no doubt that structure formation in the Mo-based complex metal oxide catalysts is indispensable for propane selective oxidation, just like as VPO catalysts [15]. Therefore, very close and regular arrangement of each catalytic functional component in the level of crystal structure or in atomic level seems to be highly important for catalyst design for the reactions. If well-arranged components are isolated structurally [4] and can complete one catalytic cycle of a selective oxidation, the resulting catalyst would be highly selective. We would like to emphasize that artificial or self-organization of catalytic components in particular structure during catalyst preparation is necessary to create new type of active sites that can achieve highly difficult selective alkane oxidations [9]. Although it is almost impossible to avoid the effect of unknown factors in catalyst preparation completely, inorganic soft synthesis, like sol–gel method, micro emulsion method, hydrothermal method, should be applied more in the preparation of complex metal oxide catalysts instead of conventional dry-up method, as could be demonstrated in this report.

3.2. Roles of each element of the MoVTeNbO(ortho) catalyst

To understand catalytic functions of the MoVTeNbO catalysts, it is highly necessary to clarify the roles of each constituent element in the selective oxidation of propane to acrylic acid, although this is normally very difficult, because changing of the elements often alters or modifies basic crystal structures. Very fortunately, however, we have recently succeeded in preparing hydrothermally the following three catalysts having different elemental compositions, binary MoVO, ternary MoVTeO and quaternary MoVTeNbO, all of which assume the same orthorhombic structure. The XRD (Cu Kα) patterns of these catalysts after the heat-treatments are shown in Fig. 2. Three catalysts showed the same main characteristic XRD peaks at 6.6°, 7.9°, 9.0°, 22.2°, 27.3° and 45.3°, all of which are ascribable to the orthorhombic structure, although the peak intensity ratios at the low angle region were slightly different in each catalyst. No other phases were detected in every catalyst.

The bulk and surface compositions of all catalysts are summarized in Table 2. ICP analysis revealed that the orthorohombic MoVO sample (designated MoVO(ortho)) had a composition of $Mo_1V_{0.34}O_x$ (Table 1). No other elements in this sample were detected besides Mo and V and particle uniformity was also ascertained by SEM analysis (data not shown) in which prism-shaped crystalline were observed. The XRD pattern (Fig. 2(1)) was nicely simulated with lattice parameter (a = 21.10Å, b = 26.57 Å and c = 4.006 Å). It has been reported that there are many structural variants in Mo–V–O system [11,12,16–18] and it can be recognized that the present structural material of MoVO is a new variant. In addition it should be pointed out that Te is no longer necessary element for the formation of the orthorhombic structure in Mo–V–O system, although it has been thought that the structure formation needs Te. Furthermore, it can be concluded that the incorporated Te into the hexagonal channel does not cause the deformation of the network in the slab, because exactly the same lattice parameter that used for MoVO could be used for the XRD simulation of the other two catalysts. In other words, the octahedra network is sustained by the corner sharing between pentagonal ring units where Mo and V are exclusively located. This was also valid from the XRD data even when Nb was introduced into the MoVTeO catalyst. This is simply due to that Nb can play the same structural role as V can do and in fact the bulk composition data determined by ICP of the MoVTeNbO sample revealed that the sum content of Nb and V in MoVTeNbO was roughly the same as the contents of V in other two samples containing no Nb (Table 2). Presumably, Nb is located at the pentagonal ring units since it is known for example that Nb is one of the elements along with Ti, V, Ta and W, which can stabilize the Mo_5O_{14}-type phase (Fig. 1(3)) by partial substitution of Mo [19].

All elements corresponding to the catalyst constituents were detected by XPS on the surface of every catalyst as

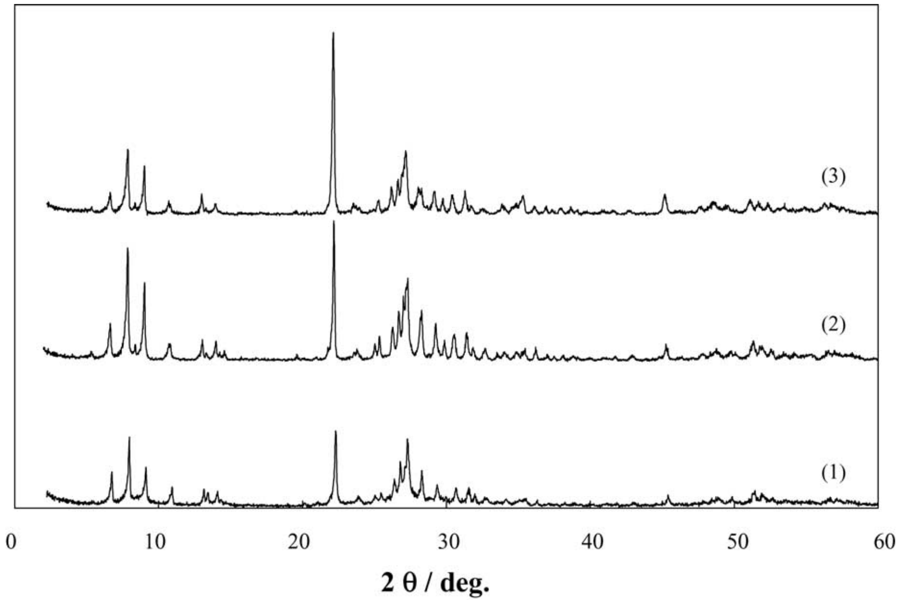

Fig. 2. XRD patterns of calcined (1) MoVO, (2) MoVTeO and (3) MoVTeNbO mixed oxide catalysts.

shown in Table 2. The surface content ratio of V/Te quite resembled to the bulk ratio in the ternary MoVTeO sample. On the other hand, the surface contents of Te and Nb in the MoVTeNbO sample were apparently higher than the bulk contents. Nb seems to be preferentially segregated on the catalyst surface at the expense of V content and the higher Te content on the surface suggests that occupancy of hexagonal center sites with Te is higher near the surface. As a consequence, the surface ratio of V/Te of this sample became appreciably lower than that in the bulk. At least two possible effects of Nb on the catalyst property can be envisaged. First, Nb can dilute V on the surface, in other words, Nb can isolate active V sites. Second, Nb may generate Mo^{5+} through redox process because Nb is 5+ and V is 4+ in the catalyst. In fact, it was observed by XPS that 7% of Mo was reduced to Mo^{5+} on the surface of the MoVTeNbO catalyst, while no reduction of Mo in the MoVTeO catalyst. All solids had similar surface areas: 6.1, 6.9 and 6.2 m^2/g for MoVO, MoVTeO and MoVTeNbO, respectively.

As a brief summary of the above results from a structural point of view, Mo and V are essential elements to form the orthorhombic structure and the octahedra network in the slab plane, whereas Te simply occupies the hexagonal channels and Nb should be regarded as a substitution element for V.

Based on the above structure information, we tried to explain the following catalytic data in order to clarify the role of each element. The three catalysts were tested in the propane oxidation to acrylic acid and the changes of both propane conversion and acrylic acid selectivity as a function of the reaction temperature are shown in Fig. 3. It is surprising to see that all these three catalysts showed almost the same oxidation activity for the propane conversion in the entire temperature range from 280 to 420 °C. Obviously the propane conversion is independent of the presence of either Te or Nb and is undoubtedly controlled by Mo and V in the particular network.

Thus, created active sites with Mo and V were, however, very poor for the formation of acrylic acid in the propane oxidation. The main products were acetic acid and CO_x, as can be seen in Table 3 which summarized all activity and selectivity data of the propane and propene oxidations over three catalysts. On the other hand, when Te was introduced in the MoVO catalysts without changing the orthorhombic structure, the resulting catalyst showed much higher selec-

Table 2
Surface and bulk composition of Mo–V–O-based catalysts

Catalyst	Composition Mo/V/Te/Nb		
	Preparative[a]	Bulk[b]	Surface[c]
MoVO(ortho)	1.0/0.25/–/–	1.0/0.34/–/–	–/–/–/–
MoVTeO(ortho)	1.0/0.5/0.16/–	1.0/0.44/0.1/-	1.0/0.36/0.08/-
MoVTeNbO(ortho)	1.0/0.3/0.16/0.12	1.0/0.25/0.11/0.12	1.0/0.18/0.19/0.17

[a] For the hydrothermal syntheses.
[b] Determined by ICP analysis.
[c] Determined by XPS analysis.

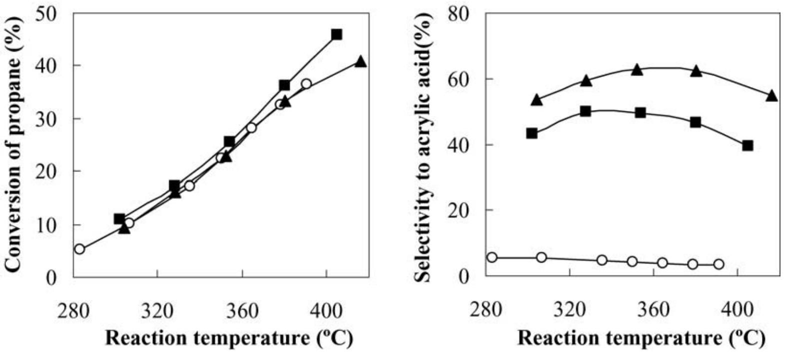

Fig. 3. Propane selective oxidation over MoVO (circle), MoVTeO (square) and MoVTeNbO (triangle) mixed oxide catalysts. Reaction conditions for the propane oxidation: 500 mg of the catalysts, total flow rate 20 ml/min and feed composition $C_3H_8/O_2/H_2O/N_2$ = 8/10/45/37 (%).

tivity to acrylic acid. Similarly when Nb was incorporated in addition to Te, the selectivity to acrylic acid improved further as clearly seen in Fig. 3.

To understand the roles of two elements Te and Nb, the overlooking of the reaction scheme is useful. The reaction scheme for the propane oxidation to acrylic acid over Mo–V–O-based catalysts has already been reported and the stepwise formation scheme through propene and acrolein has been generally accepted [5]. In both MoVTeO and MoVTeNbO catalysts, the oxidative dehydrogenation of propane to propene mainly occurs at very short contact time, indicating that propene is the first intermediate product. Then the selectivity to propene gradually goes down and selectivity to acrylic acid goes up with increasing the contact time. The selectivity, however, reaches a maximum or a steady level, because the further destructive oxidation of formed acrylic acid becomes prominent at conditions giving high propane conversions.

We thus conducted the propene oxidation over the catalysts in order to make catalytic function of Te in the propene oxidation clear. The results were listed in Table 3. Naturally all catalyst showed high activity for the propene oxidation. The following two characteristic points were observed: firstly, the MoVO catalyst revealed the lower activity for the propene oxidation than the others, in spite of that all the catalysts showed almost the same activity for the propane oxidation; secondly some amounts of acrylic acid were formed in the propene oxidation even over the MoVO catalyst which contains no Te. The two points mean that the MoVO catalyst can promote the propene oxidation to acrylic acid but needs Te to be more active and selective. This implies that Te should involve in the course of propene oxidation to acrylic acid, since it is well known that Te is one of the key elements in the allylic oxidation of olefins, like Bi.

The next point is about Nb. As shown in Fig. 3, the selectivity to acrylic acid was about 15% higher for the MoVTeNbO catalyst than for MoVTeO catalyst, especially at the high propane conversions. Beside, at very short contact time, where the overoxidation rate of acrylic acid is very low, it was observed that the product selectivities were quite similar over both catalysts. This means that the overoxidation of acrylic acid to CO_x is retarded, for instance, by the stabilization of acrylate over the Nb-containing catalyst. This role of Nb was also confirmed by the results of acrylic acid oxidation performed over both catalysts; the MoVTeNbO catalyst showed extremely lower activity for the overoxidation of acrylic acid than the MoVTeO catalyst.

This role of Nb can be interpreted on the basis of the structural information as follows. Two explanations might be formulated. The first one is so-called site-isolation [20]. Since the introduction of Nb forces the dispersion or isolation of V on the catalyst surface, the amount of active lattice oxygens which may exist around V is optimized for acrylic acid formation from propane. Then the formed acrylic acid

Table 3
Catalytic activity of orthorhombic MoV(Te)(Nb)O for the oxidations of propane and propene

Catalyst	Temperature (°C)	Conversion (%)			Selectivity (%)					
		C_3H_8[a]	C_3H_6[b]	O_2	AA[c]	C_3H_6	Ace[c]	AcA[c]	CO	CO_2
MoVO	379	32.7	–	70.1	3.4	5.1	0.2	16.9	43.9	30.5
MoVTeO	380	36.2	–	71.1	46.6	7.7	1.3	16.5	14.3	13.6
MoVTeNbO	380	33.4	–	63.8	62.4	8.7	0.4	7.3	11.1	10.1
MoVO	340	–	47.6	30.1	30.6	–	12.3	23.4	18.5	15.3
MoVTeO	342	–	56.5	26.8	55.6	–	17.3	14.2	7.6	5.3
MoVTeNbO	340	–	61.1	24.7	81.7	–	6.2	6.7	3.2	2.2

[a] Reaction conditions: 500 mg catalyst, flow rate 20 ml/min, composition $C_3H_8/O_2/H_2O/N_2$ = 8/10/45/37.

[b] Reaction conditions: 250 mg catalyst, flow rate 40 ml/min, composition $C_3H_6/O_2/H_2O/N_2$ = 3/10/45/42.

[c] AA, acrylic acid; Ace, acetone and AcA, acetic acid.

desorbs from the catalyst surface without further reaction with lattice oxygens. The second point is redox. There are redox couplings among the constituent elements except Nb. Once Nb^{5+} is incorporated into the catalyst, some reduced state like Mo^{5+} has to be formed as observed by XPS on the MoVTeNbO catalyst only and then Mo^{5+} may affect the oxidation state of the other elements Te and V through the redox couplings during the catalytic reactions. As a consequence, the concentration of active oxygen species is modulated and therefore the chance of overoxidation of adsorbed acrylic acid diminishes.

4. Conclusions

Propane selective oxidation to acrylic acid was carried out over Mo-based complex metal oxide catalyst systems, three orthorhombic catalysts having different elemental compositions, MoVO, MoVTeO and MoVTeNbO and two structurally related catalysts in order to demonstrate the importance of orthorhombic structure and to clarify the role of each elements. Most of the catalysts were prepared by hydrothermal method into a mono-phasic state. In particular, the MoVO catalyst having orthorhombic structure is a new compound that we succeeded in synthesizing by hydrothermal method. On the basis of the catalytic results, it was concluded first that structure formation in the Mo-based complex metal oxide catalysts is indispensable for propane selective oxidation, that is the structure where MO_6 (M = Mo, V) octahedra network is constructed with pentagonal and hexagonal rings of the octahedra and the heptagonal rings is generated during the linking of these pentagonal and hexagonal rings. The second conclusion is that propane molecule is oxidatively activated to propene over surface active sites constructed with Mo and V octahedra which are arranged in the high dimensional network. When Te is incorporated into the network space, the resulting catalyst becomes selective for the formation of acrylic acid without changing intrinsic oxidation activity of Mo and V sites, because Te assists propene conversion. Nb also plays an important role in increasing the selectivity to acrylic acid; Nb effectively reduces the overoxidation rate of acrylic acid. This Nb role was explained by its site isolation effect on V and by modulation effect on surface oxidation state of each element. Finally, we emphasize that high dimensional structure and the resulting multifunctionality of active sites are the key points to achieve high selectively to acrylic acid in this difficult multi-step oxidation reaction.

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